Implication of Ultra-high $\delta^{34}$S Values in Pyrite from Manganese Deposits of the Datangpo Stage, Yangtze Platform, China

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1 Geological Setting

The manganese deposits of the Datangpo stage occurred in the black rock series of the basal Datangpo Formation of the Nanhua System. Geologically, they mainly lie in the junction of the Yangtze Platform and Jiangnan Orogen. The South China Block has been formed through convergence between the Yangtze and Cathaysia blocks at ca. 1.1–0.9 Ga (Li et al., 2002; Ye et al., 2007; Li et al., 2009), which then experienced episodic rifting at ca. 820-542 Ma (Li et al., 2003; Wang and Li, 2003; Wang et al., 2009). A southeast-facing (present orientation) passive continental margin on the Yangtze Block was subsequently developed in the course of breakup of the Rodinia Supercontinent (Feng et al., 2004). Some basins controlled by the faults developed along the continental margin and to be favor for the deposition of manganese in the Datangpo stage of the Nanhua period. The ages of manganese deposits of the Datangpo stage were constrained within 662.9±4.3 to 654.5±3.8 Ma by a pair zircon U-Pb ages for the tuffaceous beds in the basal and topmost Datangpo Formation (Zhou et al., 2004; Zhang et al., 2008).

2 Deposits Descriptions

The ore-forming rocks are the black rock series of the Datangpo Formation of the Nanhua System; mainly including black carbonaceous claystone and silty carbonaceous claystone, with the thickness ranging from n-50 m. Some rhodochrosite layers occurred in the basal Datangpo Formation. The Mn layers are lenticular and stratoid, with the thickness ranging from 1-4 m. The ores have mainly micritic and microcrystal textures and massive, banded, and laminated structures. The ore minerals are mainly composed of rhodochrosite and manganocalcite and gangue minerals are composed of quartz, mica, pyrite and others. The Mn-ores are low grade with high-P and low-Fe, with the Mn content ranging from 12.44-30.03% (average 20.89%); the Mn/Fe ratios ranging from 3.46-8.90 (average 7.47); the P/Mn ratios ranging from 0.006-0.016 (average 0.008), based on the study of some typical deposits in northeastern Guizhou province and its adjacent regions (Yanglizhang, Dawu, Datangpo, Rongxi and Minle Deposit).

3 Sulfur Isotopic Composition

28 pyrite samples from 8 manganese deposits of Guizhou, Hunan, Hubei, Chongqing were selected for determination of sulfur isotope composition. The pyrite mainly shows framboidal and subhedral textures. Subhedral pyrite was selected for analyses as the framboidal pyrite was too small for separation. The $\delta^{34}$S values of pyrite range from 43.81‰-62.63‰ (average 53.26‰), which are similar to the previous studies (Li et

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Fig.1 Histogram of sulfur isotope values in pyrite from manganese deposits of the Datangpo stage.
al., 1999; Chu et al., 2003; Chen et al., 2008; Feng et al., 2010; Li et al., 2012; Zhang et al., 2010; Zhu et al., 2013). The range of $\delta^{34}$S values of pyrite is small from the single deposit (except for Guicheng) (Fig. 1), such as the $\delta^{34}$S values of pyrite from Dawu range from 43.73‰–50.89‰ (average 47.33‰), and those from Datangango range from 61.26‰–62.63‰ (average 61.38‰), which indicates the difference of deposition environment at the deposits.

4 Discussion

The pyrite with ultra-high $\delta^{34}$S values not only occurred in the basal Datangango Formation but was also reported from the Aralka Formation of the Amadeus Basin from central Australia (Hayes et al., 1992), the Nama Formation of southern Namibia (Ries et al., 2009) and the Twitya Formation of Canada (Hurtgen et al., 2002), indicating a global phenomenon. Two reasons were suggested to explain this phenomenon by the previous studies: 1) Some intercontinental seas separated from the ocean formed as a result of the breakup of the Rodinia Supercontinent. The sulphate in the sea water was reduced to H$_2$S via sulfate-reducing bacteria (BSR) without sweater supply. Thus, the residual sulfate became anomalously enriched in $^{34}$S, and led to the ultra-high $\delta^{34}$S values of pyrite. 2) A sulfate-minimum zone (SMZ) where sulphate anomalously enriched in $^{34}$S formed in the ocean in Neoproterozoic. The pyrite formed in the SMZ had ultra-high $\delta^{34}$S values.

However, some problems remain unsolved: 1) The $\delta^{34}$S values of sulphate in the sea in the early stage of the Datangango are still unknown; 2) Where is the $^{32}$S before the pyrite with ultra-high $\delta^{34}$S values formed; 3) What is the difference in sulfur isotope composition between the framboidal and subhedral pyrite?

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